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Removal of sulfur dioxide and nitrogen oxides from waste gases by wet scrubbing method

Zoran Milosevic
Lehigh University

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**REMOVAL OF SULFUR
DIOXIDE AND NITROGEN
OXIDES FROM WASTE
GASES BY WET
SCRUBBING METHODS**

**ZORAN
MILOSEVIC**

REMOVAL OF SULFUR DIOXIDE AND NITROGEN OXIDES
FROM WASTE GASES BY WET SCRUBBING METHODS

By
Zoran Milosevic

A Research Report
Presented to the Graduate Faculty
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in
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ABSTRACT

The methods of removing SO_2 and NO_x studied here included absorption of SO_2 in water, either by itself or containing catalyst, in the presence of CO as a reducing agent, as well as absorption of NO_x in sulfite solution.

Sulfur dioxide was absorbed in the form of sulfite ions. The attempts to reduce SO_2 to elemental sulfur in a wet scrubbing system were not successful, but the presence of CO appeared to increase the amount of SO_2 absorbed.

Sulfite formed during the SO_2 absorption can be used to remove NO_x from the same gas stream, provided oxygen is present. The effect is believed to be due to a higher rate of oxidation of NO in the presence of sulfite.

1. INTRODUCTION

Over the last few years a large number of processes have been proposed for the removal of sulfur dioxide from flue gases. Calculations show that total sulfur oxide emissions to the atmosphere will exceed 50 million tons/year by 1980 (1) unless good control methods are developed. Recent processes for removing SO_2 include adsorption on a solid adsorbent followed by reduction and regeneration of the adsorbent, or wet scrubbing processes in which sulfites formed upon absorption in aqueous solution are reduced to elemental sulfur using hydrogen sulfide. The IFP (Institut Francais du Petrol) process uses H_2S to form sulfite in a wet system(6). A catalytic process of reducing SO_2 to sulfur in a wet system using a reducing gas such as CO or H_2 does not yet exist.

Not much effort has been made to control emissions of nitrogen oxides (NO_x), even though some predict that by 1980 these oxides may be the primary man-made pollutant. Therefore, an effective system for simultaneous removal of SO_2 and NO_x with simultaneous recovery of elemental sulfur would be beneficial in solving both pollution problems.

In the work presented here the attempt to reduce SO_2 to sulfur using CO in a wet scrubbing reactor at 1 atm and room temperature has not yet produced promising results with the catalysts that have been investigated. But sulfite formed in these aqueous systems does increase the absorption of NO_x and, therefore, could be utilized for removing nitrogen

oxides, before being reduced to sulfur by means of H_2S . Good results were also obtained in preventing oxidation of sulfite to sulfate during experiments on the simultaneous absorption of SO_2 and NO_x by adding SO_3^- ions to the scrubbing solution.

2. GENERAL EXPERIMENTAL METHODS

The general procedure was based on measuring inlet and outlet concentrations of the gases of interest and making a material balance. Simulated flue gas was prepared by mixing NO_x and SO_2 with air and nitrogen in a mixing chamber; compositions were controlled by using rotameters and the composition of the gas mixture was monitored at the inlet and outlet of the scrubbing reactor where aqueous absorption took place. SO_2 was collected by an H_2O_2 solution followed by titration; NO_x was monitored by a chemiluminescent detector; CO was analyzed by an electrochemical detector. The total volume of the gas passed through the reactor was either measured by a wet gas meter (if the gas of interest was not soluble in water) or calculated from a known flow rate and measured time. The scrubbing reactor was operating at 1 atm. and temperatures ranging from 20°C to about 90°C using an electrically heated bath to keep the reactor at a desired temperature. A schematic diagram of experimental apparatus is shown in Figure 1.

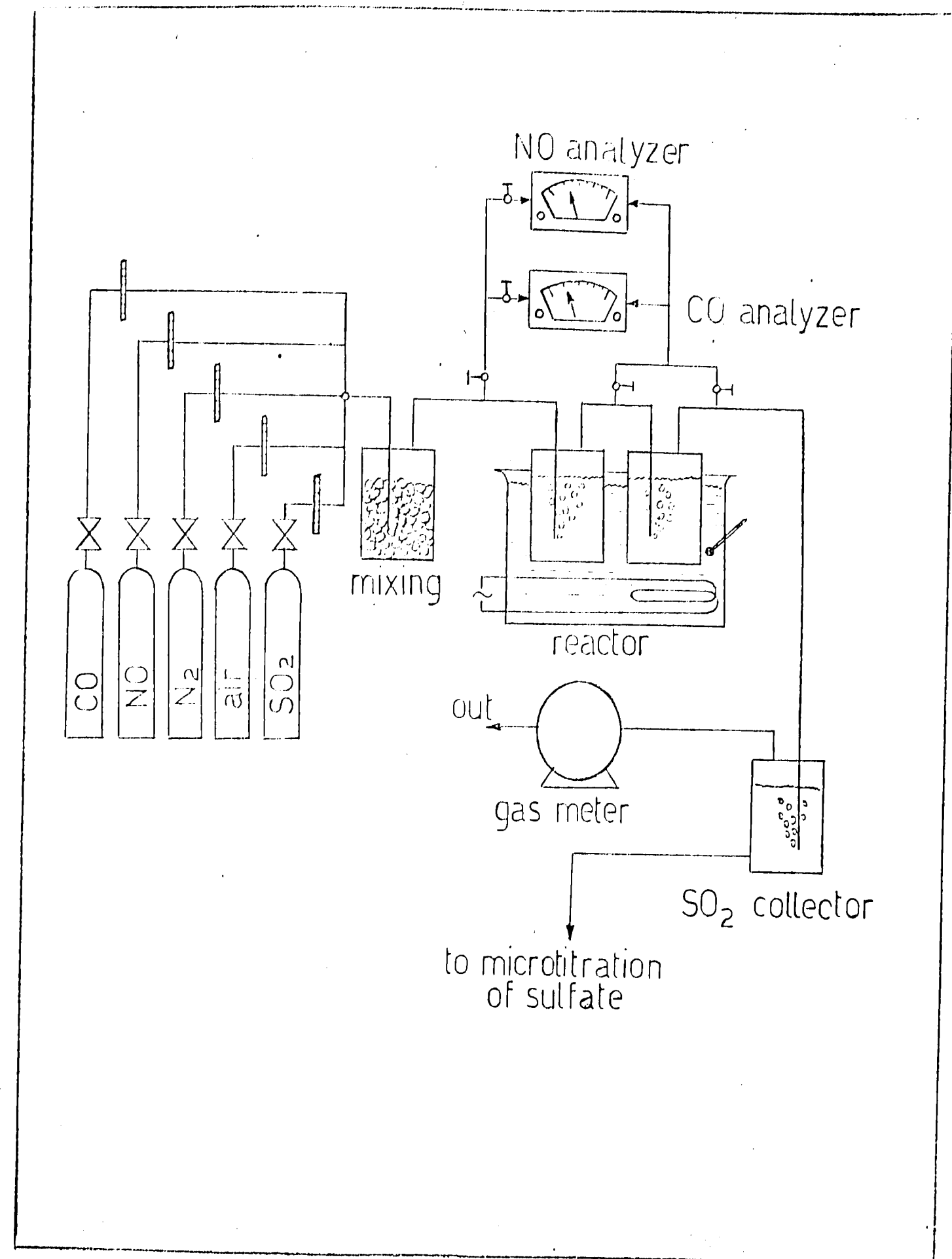
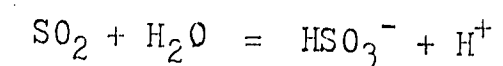


FIGURE 1. Experimental apparatus

3. SO₂ SCRUBBING EXPERIMENTS

3.1. INTRODUCTION

The solubility of sulfur dioxide in water is limited. It dissolves and reaches equilibrium as follows:



Obviously the solubility can be increased by removing the hydrogen ions formed either by using a basic absorbent or by the buffering action of various reagents such as citrate and phosphate dissolved in water. This is the underlying basis for various processes under development for removing large amounts of SO_2 from flue gases (5,6,7). Sulfite formed by dissolution of SO_2 in water can be reduced to elemental sulfur using H_2S in another reactor.

It appeared in the present work that the tendency of SO_2 to readily form sulfite in aqueous solution makes it very difficult to reduce it directly to elemental sulfur in a wet scrubbing system. In all such attempts a sulfite has been formed but the reducing agent (CO) has not had any effect. It was found, however, that the presence of CO can increase the removal of SO_2 from the gas stream; the mechanism of this phenomenon is not yet fully understood.

On the other hand, formation of sulfite is desirable since, as it will be shown later, its presence increases greatly the removal of NO_x .

Because of this it is likely that a sulfite-forming process (such as the citrate process) will also be beneficial for removing NO_x from flue gases.

3. 2. EXPERIMENTAL METHODS

As shown in Figure 1., the outlet concentration of SO_2 is determined by passing the gas through an SO_2 collector, a 3% hydrogen peroxide solution wherein all SO_2 is oxidized to sulfuric acid. This solution is then analyzed by microtitration of sulfate (2), using barium perchlorate and Thorin /2(2-hydroxy-3,6-disulfo-1-naphthylazo) benzenearsonic acid/ as the indicator. Since this is an integral method of analysis, the time and flow rate of SO_2 must be measured to determine average concentrations in the outlet gas stream. This method was sufficiently accurate to compare the performances of different catalysts and absorbing agents operating at the same conditions, but not well suited for kinetic studies.

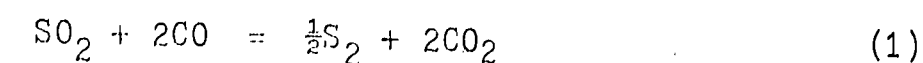
Carbon monoxide concentration was monitored by a CO-analyzer (Ecolyzer(s)-Energetics Science, Inc.) based on an electrochemical process involving CO and an aqueous electrolyte on a catalytically active electrode. Relatively high interference of SO_2 was a limiting factor and smaller sulfur dioxide concentrations had to be used when analyzing for CO. As the influence of CO on SO_2 absorption was of greatest interest, this was not a serious problem.

The scrubbing reactor consisted of two half-liter bubblers placed within an electrically heated bath to obtain controlled operating temperatures between 20°C and 90°C . Scrubbing catalysts were either dissolved in the aqueous scrubbing solution or suspended therein in the case of insoluble catalyst. Ordinarily, the bubbling gas caused sufficient agitation to keep the catalyst particles uniformly dispersed throughout the reactor. If that was not the case gentle agitation was provided by a magnetic stirrer.

In attempts to reduce SO_2 to sulfur using CO by passing the gases through catalyst-containing water the following catalysts were investigated: activated bauxite, zinc ferrite spinel (ZnFe_2O_4), magnesium ferrite spinel (MgFe_2O_4), red and black copper oxide, black cobalt oxide and alumina. All of these were used in the form of a fine powder suspended in the aqueous scrubbing solution. Sodium formate and citric acid were used in attempts to reduce SO_2 or SO_3^\pm to elemental sulfur. This was done using the latter reagents dissolved in an aqueous solution containing platinum-on-alumina and rhodium-on-alumina catalysts in suspension.

3.3. THERMODYNAMICS

The reaction between SO_2 and CO can be written:



But this is accompanied by the reaction:



Lepsoe (3) has published expressions for the free energy changes ΔG_1^0 and ΔG_2^0 of reactions (1) and (2) in terms of the absolute temperature:

$$\Delta G_1^0 = -51760 + 2.75 \cdot \ln T - 2.8 \cdot 10^{-3} T^2 - 3.1 \cdot 10^{-7} T^3 + 8.2 \cdot T$$

$$\Delta G_2^0 = -22500 + 21.0 \cdot T$$

where ΔG is in units of calories/gmol and T is in units of degrees Kelvin.

The equilibrium constants for reactions (1) and (2) are:

$$K_1 = \frac{/\text{S}_2/\frac{1}{2} \cdot /\text{CO}_2/2}{/\text{SO}_2/ \cdot /\text{CO}/2}$$

and:

$$K_2 = \frac{/\text{COS}/}{/\text{S}_2/\frac{1}{2} \cdot /\text{CO}/}$$

where $/\text{SO}_2/$, $/\text{CO}/$, $/\text{S}_2/$, $/\text{CO}_2/$ and $/\text{COS}/$ are the equilibrium concentrations of the gases.

The relationship between K and ΔG^0 is expressed as:

$$\log K = \frac{\Delta G^0}{2.303 RT}$$

giving the following expressions for K_1 and K_2 :

$$\log K_1 = \frac{11300}{T} - 1.375 \log T + 6 \cdot 10^{-4} T - 7 \cdot 10^{-8} T^2 - 1.77$$

$$\log K_2 = \frac{4920}{T} - 4.6$$

The temperature dependence of K_1 and K_2 is shown in Figure 2. where it is evident that both reactions are thermodynamically feasible, especially at lower temperatures.

This analysis shows that at low temperatures reaction (2) has a very large equilibrium constant indicating that essentially all S_2 formed in reaction (1) might react with an excess of carbon monoxide to form unwanted COS.

This may be the reason that no detectable amounts of sulfur were formed; we did not analyze for COS.

A selective catalyst that will enhance reaction (1) but not reaction (2) does not appear to be known.

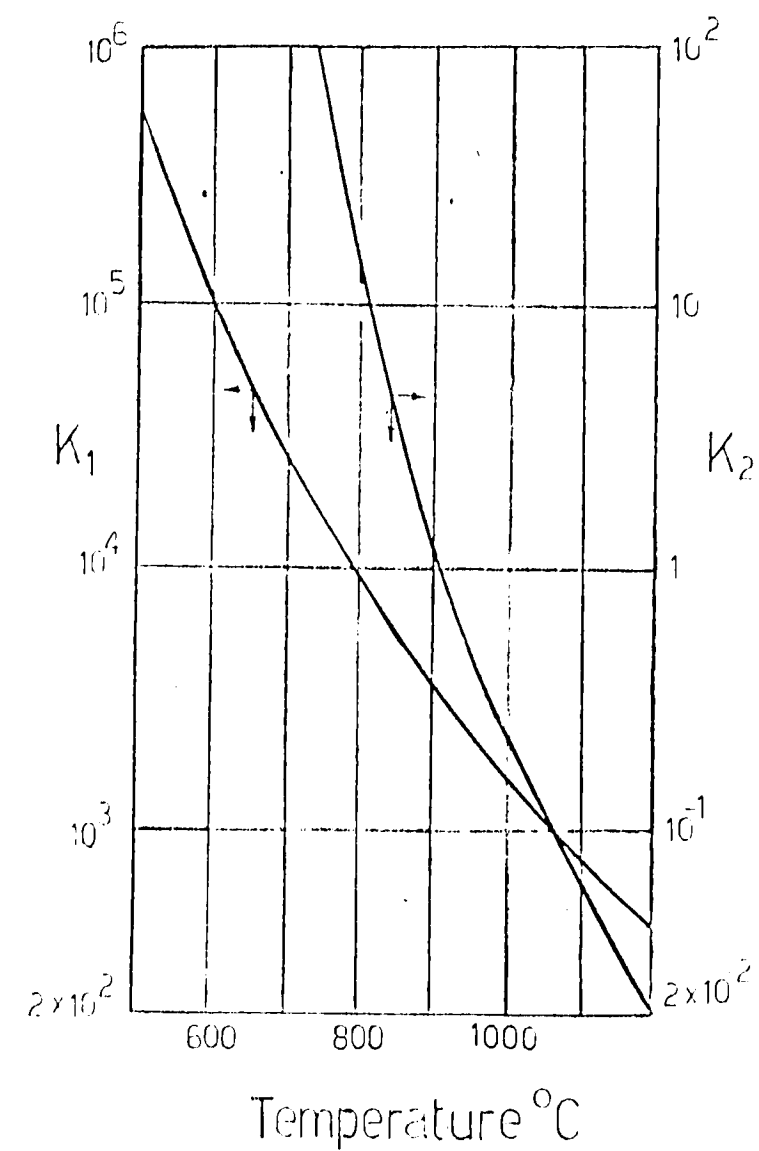


FIGURE 2. Relationship between equilibrium constants and temperature

3.4. EXPERIMENTS AND RESULTS

In the first set of experiments the solubility and efficiency of removal of SO_2 by water solutions and suspensions of different catalysts were investigated. All experiments were repeated with and without the presence of carbon monoxide. The SO_2 concentrations were maintained between 2000 and 6000 ppm and the amount of CO ranged from the stoichiometric value ($\text{CO}/\text{SO}_2 = 2$) up to about 5%. The gas mixture was passed through the reactor (in this case a single half-liter bubbler) at flow rates between 1000 and 4000 ml/min. SO_2 was then collected by bubbling through H_2O_2 solution (Figure 1) from which a 1-ml sample was taken every 15 min. and analyzed for sulfate. Both air and pure nitrogen as well as various N_2/O_2 mixtures were used as carrier gas (i.e. simulated flue gas).

The presence of copper oxides or of zinc and magnesium ferrites appeared to promote the formation of sulfites or, in the presence of oxygen, sulfates. In every case the presence of CO in the gas stream increased the removal of SO_2 if catalyst was present.

EXP. 1

$t = 20^\circ\text{C}$; $p = 1 \text{ atm.}$

catalyst: ZnFe_2O_4 (2 gm)

gas mixture: air with 3400 ppm SO_2

flow rate: 2800 ml/min

volume of water in the reactor: 500 ml

| time, min. | 0 | 15 | 30 | 45 |
|---|---|-----|-----|-----|
| amount of SO_2 in collector, ml @ 20°C | 0 | 4.3 | 130 | 270 |
| pH in reactor | 9 | 2.3 | 1.9 | 1.9 |

EXP. 2

T = 20°C ; P = 1 atm.

catalyst: ZnFe_2O_4 (2 gm)

gas mixture: air with 3400 ppm SO_2 and 7000 ppm CO

flow rate: 2800 ml/min

volume of water in the reactor: 500 ml

| | | | | |
|---|---|-----|-----|-----|
| time, min. | 0 | 15 | 30 | 45 |
| amount of SO_2 in collector, ml @ 20°C | 0 | 1 | 10 | 80 |
| pH in reactor | 9 | 2.3 | 1.9 | 1.9 |

The results of these two experiments are shown plotted in Figure 3. The outlet SO_2 concentration is calculated by dividing the accumulated amount of SO_2 (between taking two samples) by the time interval. The curve for water alone under the same conditions as in EXP. 1 is also shown. Without the presence of a catalyst carbon monoxide did not have much effect on SO_2 sorption.

EXP. 3

This was the same as EXP. 2 but using nitrogen instead of air.

| | | | | | |
|---|---|-----|-----|-----|-----|
| time, min. | 0 | 15 | 30 | 45 | 60 |
| amount of SO_2 in collector, ml @ 20°C | 0 | 1 | 22 | 110 | 270 |
| pH in reactor | 9 | 4.3 | 2.6 | 2.4 | 2.4 |

The pH of the solution in the reactor is higher without oxygen because essentially no sulfuric acid was formed. The values of pH in experiments 2 and 3 are plotted in Figure 4. In experiments 1 and 2 large amounts of ferric ions were detected using sodium thiosulfate (violet-red color that disappears quickly is typical for Fe^{+++}). No ferric ions were detected in EXP. 3.

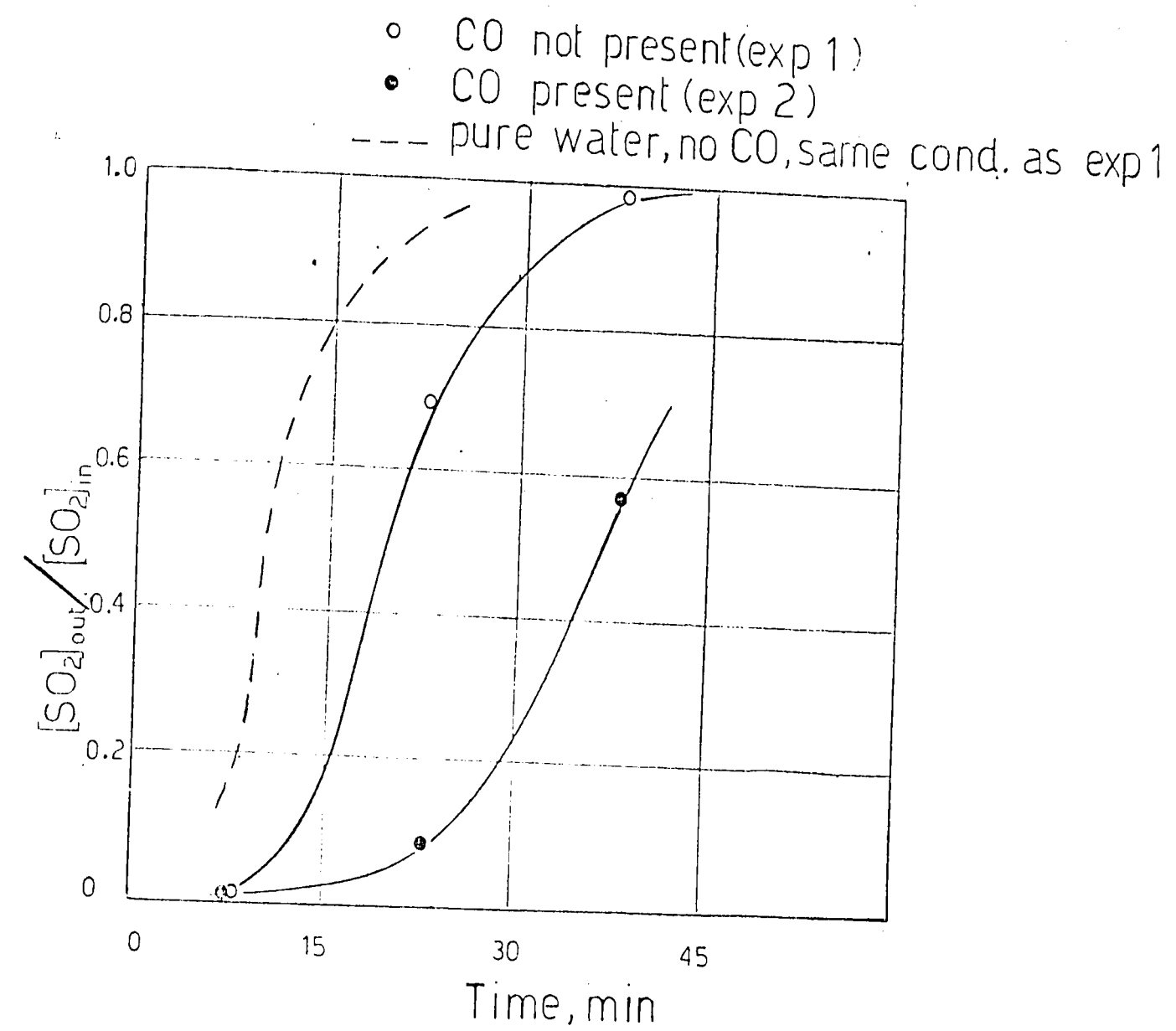


FIGURE 3. Influence of CO on SO₂ absorption

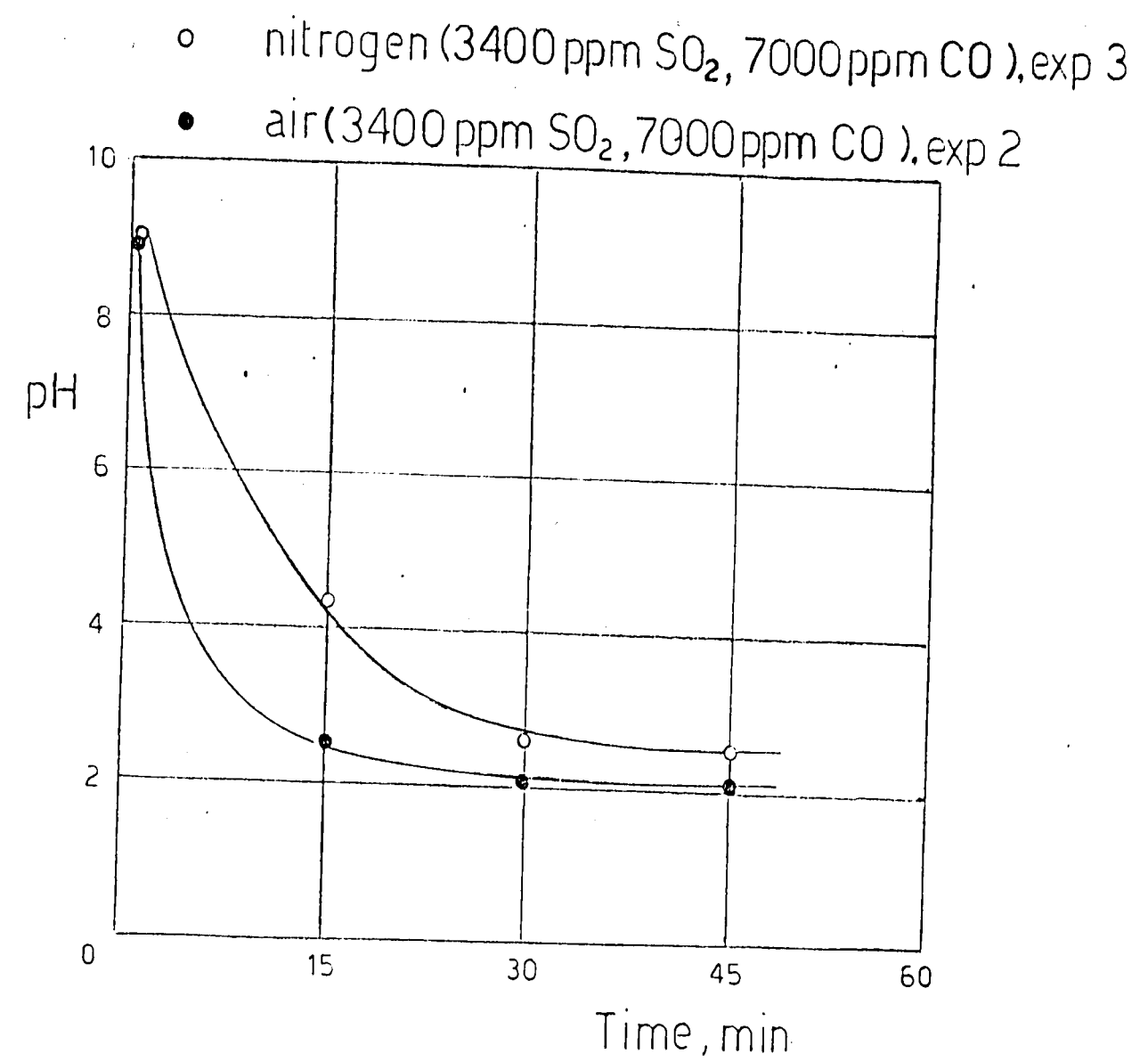


FIGURE 4. Influence of oxygen on pH

Copper oxide causes the removal of larger amounts of SO_2 and, in the presence of CO, even more, as is shown in EXP. 4 & 5.

EXP. 4

T = 20°C ; P = 1 atm.

catalyst: CuO red

gas mixture: nitrogen with 4000 ppm SO_2 and 8000 ppm CO; no oxygen

flow rate: 2400 ml/min

volume of water in the reactor: 500 ml

| | | | | |
|---|----|----|-----|----|
| time, min. | 15 | 30 | 45 | 60 |
| amount of SO_2 in collector, ml @ 20°C | 0 | 0 | 4.3 | 35 |
| final pH = 4.0 | | | | |

EXP. 5

The same as EXP. 4, but no CO present in the gas mixture.

| | | | | |
|---|----|----|----|----|
| time, min. | 15 | 30 | 45 | 60 |
| amount of SO_2 in collector, ml @ 20°C | 0 | 17 | 38 | 77 |
| final pH = 2.7 | | | | |

The reactor solution became blue during these experiments (EXPS. 4 & 5) indicating presence of copper salts.

The difference in final pH with and without CO present in the flue gas might indicate that less free H_2SO_3 is formed and that the SO_2 ultimately becomes a copper salt or even sulfur and COS due to the reducing action of carbon monoxide. Since no oxygen was present in experiments 4 & 5, no carbonates could have been formed from CO but, in experiments 1 & 2, formation of carbonates might have occurred thereby increasing SO_2 removal by buffering action.

The influence of SO_2 on CO absorption in a scrubbing solution containing catalyst was also investigated in EXP. 6:
EXP. 6

$t = 20^\circ\text{C}$; $p = 1 \text{ atm}$

catalyst: ZnFe_2O_4 (2 gm)

gas mixture: air with 550 ppm of CO

flow rate: 2000 ml/min

volume of water in the reactor: 500 ml

Since the solubility of CO in water is very low, the outlet concentration approaches the inlet concentration more rapidly than in the case of SO_2 . In Figure 5. is shown the effect of opening the SO_2 -valve thereby admitting SO_2 to the inlet gas (about 10 ml/min)- this causes the outlet concentration of CO to fall thereby further suggesting reaction between SO_2 and CO. Because of the high interference of SO_2 on CO concentration measurement by the particular instrument employed to detect CO this experiment was conducted for a short time only: as long as no SO_2 could be expected in the outlet stream entering the CO detector.

Since in all these experiments no elemental sulfur was detected as a reaction product, another set of experiments was done, wherein pure CO and SO_2 in different ratios were drawn through the reactor containing water and a catalyst. The same catalysts as before were used with reactor temperatures ranging from 20°C to 90°C , with flow rates from 2000 to 5000 ml/min, and for periods ranging from 1 to 24 hours. The solids that were present (mixed with catalyst particles) after shut down were

treated with carbon disulfide to dissolve any elemental sulfur that might be present. The carbon disulfide was then filtered and allowed to evaporate. The residue from evaporating CS_2 showed no detectable amounts of sulfur. The use of sodium formate, formic acid or acetic acid solutions instead of pure water, with platinum-on-alumina and rhodium-on-alumina catalysts, did not indicate formation of sulfur in similar experiments.

The results of experiments 1, 2 and 3 using MgFeO_2 and ZnFe_2O_4 in attempting to promote reaction of CO and SO_2 in the wet scrubbing reactor are typical with respect to the change of the SO_2 outlet concentration versus time. Each of the other catalysts gave approximately the same results except for the red copper oxide which caused greater SO_2 removal, but presumably because it reacted with the SO_2 or with CO to form a buffer instead of behaving as a catalyst as intended.

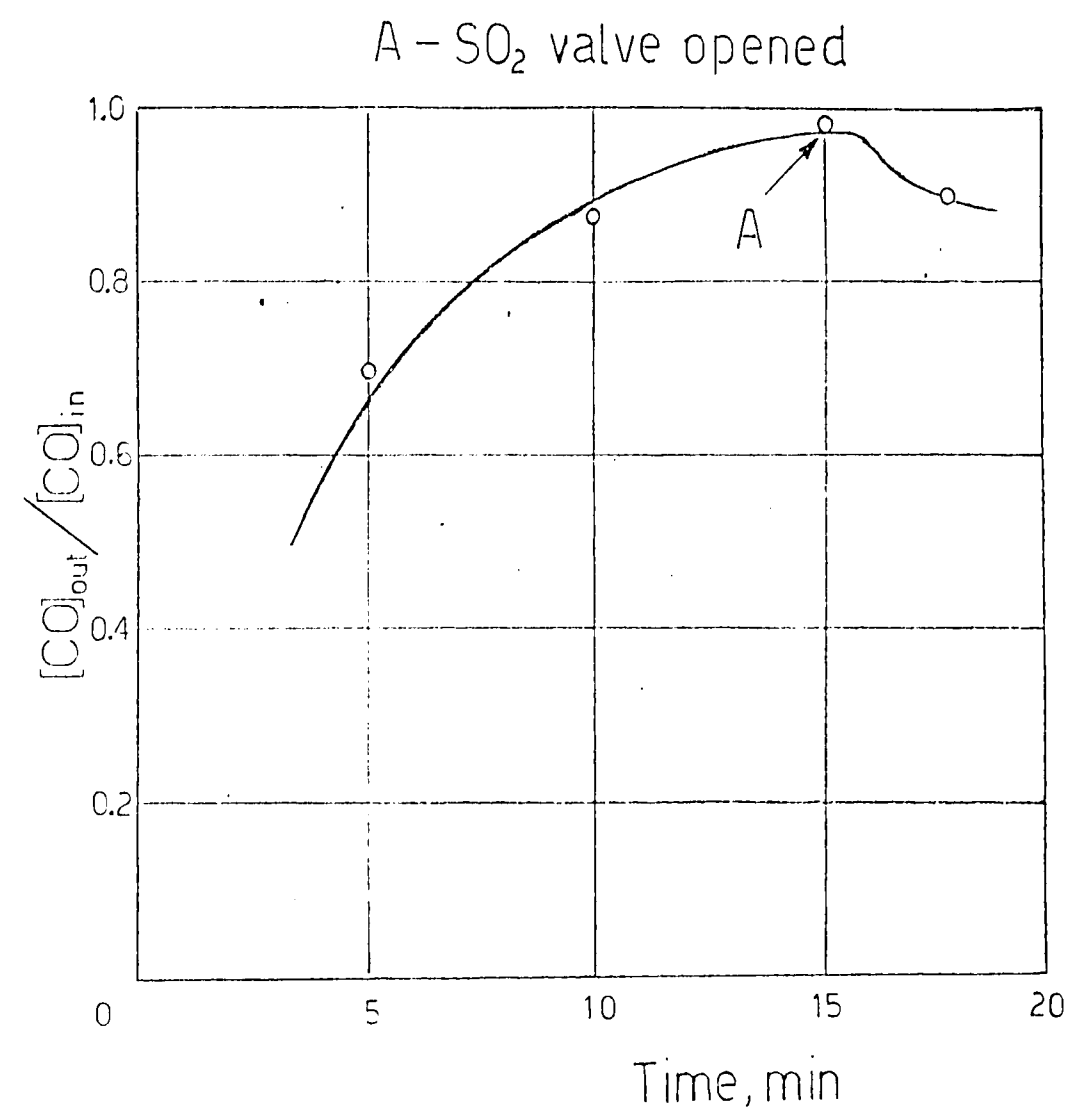


FIGURE 5. Influence of SO₂ on CO absorption

3.5. DISCUSSION AND RESULTS

The most important information obtained to date by the experiments described here is the influence of CO upon SO_2 sorption. In the system that was used here, carbon monoxide with concentrations not higher than those that might be expected in real situations increased the amount of SO_2 adsorbed by significant amounts.

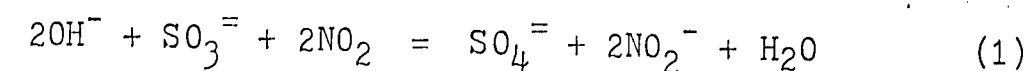
Future experiments will be aimed at obtaining more information using a photometric SO_2 analyzer by which instantaneous concentrations of SO_2 in the gas can be measured. This will permit almost instantaneous determination of the effect of SO_2 absorption of suddenly admitting CO to the gas stream. By combining the photometer analyzer with a gas chromatograph it should also be possible to observe whether COS is formed.

Future and continuing experiments will attempt to explain the exact influence of CO, i.e. whether it enhances SO_2 absorption by merely forming a carbonate buffering agent or whether it actually reacts with SO_2 to form a product such as COS. Future work will also continue to seek catalysts for promoting the reaction of CO and H_2S with SO_2 in aqueous solution.

4. NO_x SCRUBBING EXPERIMENTS

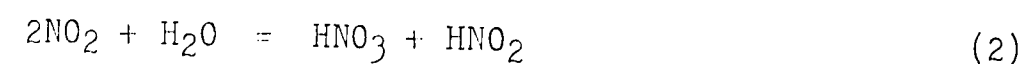
4.1. INTRODUCTION

The basic method studied here is the use of an aqueous solution of sulfite to remove NO_x ($\text{NO} + \text{NO}_2$) from a gas stream. It will be shown that NO_2 reacts with SO_3^- to form SO_4^- and NO_2^- :

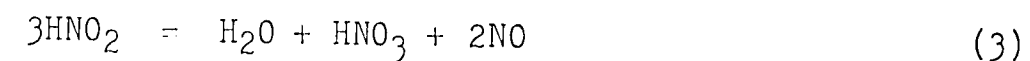


The resulting nitrite ion may then be oxidized to nitrate ion by the oxygen present in the gas stream.

Nitrogen dioxide (NO_2) is also very soluble in pure water where it forms nitrous and nitric acids:

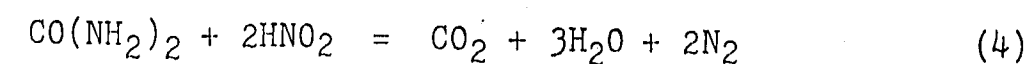


and the nitrous acid may then react with O_2 to form nitric acid. Nitric oxide (NO) is formed during this process:



Nitric oxide is practically insoluble in water and only slightly soluble in SO_3^- solution but, as it will be shown, sulfite can significantly increase the NO absorption if oxygen is present. This effect is believed to be due to a higher NO oxidation rate and absorption of the product (NO_2).

In this work an attempt was made to use urea $\text{CO}(\text{NH}_2)_2$ to decompose nitrous acid and hereby prevent the evolution of NO in the reactor according to reaction (3). The reaction with urea is:



but this reaction was found to be very slow under the experimental conditions.

The sulfite ion used to remove NO_x could be obtained by dissolving sodium sulfite (Na_2SO_3) in water, or by bubbling SO_2 through water.

The oxidation of sulfite by oxygen present in the gas stream is undesirable because sulfate formed this way was found not to have any effect on NO_x absorption. Especially at higher temperatures (70°C) sulfite disappears very quickly and NO_x outlet concentrations then increase accordingly.

It will be shown that the addition of sulfate to the water in the reactor can slow down the SO_3^- oxidation. It is believed that this phenomenon may be interpreted in terms of diffusion of the SO_4^- produced at the bubble surface into the bulk solution as the rate controlling step. By increasing SO_4^- concentration in the bulk, the driving force was reduced.

The apparatus was the same as used for the SO_2 scrubbing experiments as shown in Figure 1. but the SO_2 collector was not needed.

4.2. EXPERIMENTAL METHODS

The NO_x inlet and outlet concentrations were measured by means of a chemiluminescent NO-NO_x gas analyzer (THERMO ELECTRON, Model 10-B).

The absorption of both NO and NO_x was investigated. If pure nitrogen was used as a carrier gas there could not have been any NO_2 present in the gas stream since only NO was feed. With the feed of NO in air the NO was partly oxidized to NO_2 before entering the reactor. A problem arose in measuring NO_x flow rates. Since NO_2 boils at 70°F at a pressure of one atmosphere, the flowmeter was ineffective because droplets of liquid (N_2O_4) formed inside the tube. Because of this the NO_x concentrations were controlled by opening valve until the desired concentration of either NO or NO_2 was obtained at the inlet in the reactor.

The concentrations of NO_2^- and NO_3^- in water were measured by a colorimetric water analyzer (DELTA SCIENTIFIC, Model 260) using naphthylamine and Brucine sulfanilic acid as color reagents.

A solution of KMnO_4 containing sulfuric acid was used to detect $\text{SO}_3^{=}$ ions and determine the sulfite life time in water through which the air is bubbled. KMnO_4 solution is decolorized by sulfites but also by nitrous acid so this test had to be made separately and not in the same reactor where NO_x was absorbed.

In the experiments with urea, potassium iodide was used to detect the presence of nitrous acid. If nitrite ion is added to a solution of potassium iodide (4) and the solution is

acidified with sulfuric acid, the solution becomes yellow, owing to the formation of iodine and is colored blue if a little starch paste is added. The test does not work in the presence of sulfite because SO_3^- reacts immediately with the iodine formed.

4.3. THERMODYNAMICS

Nitric oxide is oxidized to nitrogen dioxide according to the reaction:



The standard free energy change of this reaction at 20°C and one atmosphere is:

$$\Delta G^\circ = \Delta G^\circ_{\text{NO}_2} - \Delta G^\circ_{\text{NO}} = 12390 - 20719 = -8329 \text{ cal/gmol}$$

and the equilibrium constant:

$$K_o = e^{-\frac{\Delta G^\circ}{RT_o}} = e^{-\frac{8329}{1.98 \cdot 293}} = 17.2 \times 10^5$$

The heat of reaction at 20°C is:

$$\Delta H^\circ = \Delta H^\circ_{\text{NO}_2} - \Delta H^\circ_{\text{NO}} = 8041 - 21600 = -13559 \text{ cal/gmol}$$

Assuming that ΔH° will not change much in the range 20-70°C that has been investigated, we get the temperature dependency of the equilibrium constant from the van't Hoff equation:

$$d(\ln K) = \frac{\Delta H^\circ}{R} \frac{dT}{T^2}$$

Integrating from $T_o = 293^\circ\text{K}$ to T :

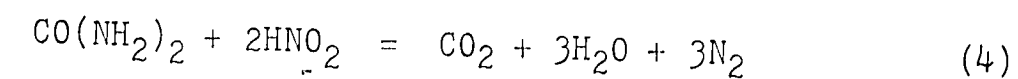
$$\ln \frac{K}{K_o} = \frac{13559}{1.98} \left(\frac{1}{T} - \frac{1}{T_o} \right)$$

$$\ln K = \ln K_o - 6848 \left(\frac{1}{293} - \frac{1}{T} \right)$$

Since the second term in this expression is not big and K_0 is large, we can assume an irreversible reaction throughout the operating range. This is important in that it tells that, if chemical reaction were the rate limiting or controlling step, then removal of the product (NO_2) would not significantly reduce the NO concentration in the outlet any further.

Urea - Nitrous Acid Reaction

It is known (4) that urea will react with nitrous acid to form CO_2 , H_2O and N_2 :



The free energy change of this reaction at 20°C is:

$$\Delta G^0 = \Delta G_{\text{CO}_2}^0 + 3\Delta G_{\text{H}_2\text{O}}^0 - \Delta G_{\text{urea}}^0 - 2\Delta G_{\text{HNO}_2}^0$$

$$\Delta G^0 = -217.88 - 2\Delta G_{\text{HNO}_2}^0 \quad (\text{Kcal/gmol})$$

Since nitrous acid does not exist in pure form, it is difficult to obtain data as to its free energy of formation, values of which will depend strongly on the degree of hydration and could vary from case to case. The value of ΔG^0 of reaction (4) above could be positive with a correspondingly low equilibrium constant and low conversion if the free energy of formation of HNO_2 is sufficiently negative.

4.4. EXPERIMENTS AND RESULTS

The experimental procedure was to bubble NO or NO_x through water, either pure or containing SO₃⁼ ions, with measurement of the difference in inlet and outlet gas concentrations. The sulfite ions were formed either by dissolving sodium sulfite (Na₂SO₃) in water or by bubbling SO₂ through water. The inlet NO_x concentrations were maintained between 1000 and 6000 ppm with flow rates 1300-1200 ml/min.

Since the solubility of NO in pure water is very low it was sometimes more convenient simply to compare the NO concentrations in effluent gas from a reactor containing only pure water with the effluent concentrations from a reactor containing sulfite solution. This was possible, however, only when nitrogen was used as a carrier since the NO is oxidized when air is the carrier gas, and there were indications that the oxidation rates are not the same in the sulfite solution as in pure water.

It was found that, in the absence of oxygen, sulfite solution does not absorb much NO but does absorb large amounts of NO₂. When 400 ml/min of 1100 ppm NO in nitrogen at room temperature were passed through a 500 ml bubbler containing water and 4 gm Na₂SO₃ the outlet NO concentration was 950 ppm. A somewhat better result was obtained when SO₂-saturated water was used but the gas stream in this case strips out some of the dissolved SO₂ and the outlet NO concentration drops, apparently due to dilution by the stripped SO₂. After 20-40 min the NO concentra-

tion in the effluent again increases to about 800 ppm (which is lower than the concentration at the outlet of the Na_2SO_3 -containing reactor), but this improvement in NO removal can be ascribed to the change in pH of the solution (sodium sulfite is basic and the SO_2 solution acidic).

Using air instead of nitrogen at the same flow rate and reactor volume and opening the NO valve until the inlet concentration reaches 1100 ppm NO (we need about 2000 ppm for this because a part of it is oxidized to NO_2 in the lines, so NO_x at the inlet is 2000 ppm), the concentrations at the outlet of the pure water reactor were:

$$\text{NO} = 700 \text{ ppm}$$

$$\text{NO}_2 = 300 \text{ ppm}$$

Since NO is not sufficiently soluble in water to account for the low effluent NO concentration the difference can be explained in terms of oxidation of NO to NO_2 within the reactor and absorption of the latter.

When the pure water was replaced by a sodium sulfite solution (8 gm/liter) of the same volume (500 ml) the outlet concentrations dropped to:

$$\text{NO} = 450 \text{ ppm}$$

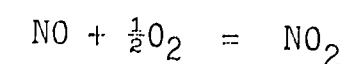
$$\text{NO}_2 = 120 \text{ ppm}$$

and they remained constant until the sulfite was oxidized to sulfate by the air (about 120 min at the given flow rate of 400 ml/min).

This simple experiment shows that NO_2 can be removed in significant quantities from a gas stream using sulfite solution. Also with oxygen present, sulfite is a good NO absorbent. Since sulfite solution does not remove such substantial amounts

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of NO from a mixture with oxygen-free nitrogen, a possible explanation is that SO_3^- ions enhance the NO oxidation and then the oxidation product, NO_2 is absorbed. It was shown that the reaction:



has a very large equilibrium constant; removing its product therefore cannot significantly shift the reaction to the right and thereby reduce the NO partial pressure. Thus the explanation cannot be in terms of an equilibrium shift and thereby suggests an increase in the rate of the NO oxidation due to the presence of SO_3^- ions.

It should be emphasized that the bubble size changes when sulfite solution is used instead of water (it decreases about twice when 4 gm of sodium sulfite are added) but the gas-liquid contact area is not important for homogeneous NO oxidation by the oxygen in air; in the present case where the SO_3^- in the liquid may act as a catalyst, the bubble size and gas-liquid interfacial area could have an important influence on the rate. The effect would not disappear after all the sulfite was oxidized to sulfate, however, if it was only the bubble size that made the difference.

The same experiment was repeated with different inlet concentrations. The results are shown in Table 1.

It is evident that in all cases the presence of sulfite was associated with reduced outlet concentrations of both NO_2 and NO. But this effect lasted for a relatively short time only. i.e., until the sulfite was oxidized to sulfate by the oxygen present in the air. The next two experiments show the change of NO and NO_2 outlet concentrations vs. time at two dif-

| Exp. # | Carrier Gas | NO Inlet ppm | NO ₂ Inlet ppm | Pure Water | | | 8 gm/liter Sulfite Solution | | | Flow Rate ml/min | Temp. °C |
|--------|-------------|--------------|---------------------------|------------|---------------------|---------------------------|-----------------------------|---------------------|---------------------------|------------------|----------|
| | | | | NO Out | NO ₂ Out | % NO _x Removed | NO Out | NO ₂ Out | % NO _x Removed | | |
| 1 | Air | 2100 | 3300 | 1400 | 1000 | 56 | 1000 | 400 | 80 | 800 | 20 |
| 2 | Air | 2100 | 1900 | 1500 | 650 | 46 | 850 | 100 | 76 | 1200 | 20 |
| 3 | Air | 2500 | 2000 | 2400 | 800 | 29 | 1350 | 200 | 65 | 850 | 70 |
| 4 | Air | 3000 | 2000 | 2300 | 1300 | 28 | 1600 | 250 | 63 | 700 | 20 |
| 5 | Air | 2000 | 2500 | 1500 | 1000 | 44 | 1000 | 200 | 73 | 550 | 40 |
| 6 | Air | 1400 | 1500 | 800 | 300 | 62 | 400 | 100 | 82 | 1000 | 20 |

TABLE 1.

ferent temperatures.

EXP. 7

gas mixture: air + 2100 ppm NO + 3300 ppm NO₂

flow rate: 800 ml/min

Na₂SO₃ concentration: 8 gm/liter

temperature: 20°C

volume of the reactor: 500 ml

| | | | | | | | | | |
|-------------------------|------|-----|-----|-----|-----|------|------|------|------|
| time, min | 2 | 10 | 20 | 30 | 40 | 55 | 65 | 80 | 90 |
| NO out ppm | 1000 | 950 | 950 | 900 | 950 | 1650 | 2000 | 2000 | 2000 |
| NO ₂ out ppm | 100 | 100 | 100 | 100 | 100 | 950 | 1000 | 1200 | 1200 |

EXP. 8

gas mixture: air + 2500 ppm NO + 2000 ppm NO₂

flow rate: 850 ml/min

Na₂SO₃ concentration: 8 gm/liter

temperature: 70°C

volume of the reactor: 500 ml

| | | | | | | | | |
|-------------------------|------|------|------|------|------|------|------|------|
| time, min | 2 | 5 | 10 | 15 | 20 | 25 | 30 | 40 |
| NO out ppm | 1350 | 1350 | 1400 | 1500 | 1800 | 2400 | 2400 | 2400 |
| NO ₂ out ppm | 200 | 200 | 200 | 200 | 400 | 800 | 900 | 900 |

The foregoing experiments show that the effect of sulfite disappears after about 55 min at 20°C and 20 min at 70°C. Another experiment showed that when only air was bubbled through the same sulfite solution as in Experiments 7 and 8, and at the same flow rates, the sulfite disappeared after 100 min at 20°C and after 30 min at 70°C. Sulfite was analyzed using KMnO₄.

It is obvious that oxidation of sulfite by the oxygen in the air is the determining factor in the efficiency of NO_x absorption by sulfite and that the rate of this oxidation has to be decreased as much as possible if the overall process is to be usefully harnessed.

In experiment 8 (at 70°C) after Na_2SO_3 had been completely oxidized, the NO concentration goes up to 2400 ppm which is the outlet concentration for a pure water reactor at 70°C (see Table 1, exp. 3). This concentration is also close to that of the inlet, thereby indicating that at higher temperatures NO is much less oxidized to NO_2 . In experiment 7, which was at a lower temperature (20°C), the NO outlet concentration rises above the pure water (at 20°C) outlet concentration (400 ppm as shown in Table 1, exp. 1). This behaviour could be explained by the fact that the temperature of 20°C is very close to the NO_2 boiling temperature at 1 atm and only a slight temperature change (due to the heat of reaction liberated by SO_3^- oxidation) could make a big difference in the NO_2 behaviour. Different experiments at the same temperature (20°C) showed that after all sulfite was oxidized, the NO outlet concentration rose up to a value approx. 500 ppm higher than it would be with pure water at 20°C , and after some time (30-40 min) it went down again. This effect of NO out exceeding the pure water outlet concentration was not observed at 70°C because this temperature is far above the NO_2 boiling point. It is still not understood how the NO_2 phase change can affect the NO oxidation rate.

The dissolved products of NO_x scrubbing both by pure water and Na_2SO_3 solution were found to be nitrate and nitrite. Since the oxidation of nitrite to nitrate is accompanied by evolution of NO that might escape from the reactor, it would be desirable to decompose the nitrite before it is oxidized. Urea is known to decompose nitrous acid and, since all the nitrite must have been originally in the form of nitrous acid when pure water was used as scrubber liquid, we tried to improve the NO absorption by dissolving some urea in the water. But this did not reduce the NO level at the outlet and the solution contained the same amount of nitrous acid. As discussed before, the degree of hydration of nitrous acid might be critical in determining whether the free energy change of the urea-nitrous acid reaction would be positive or negative. It is likely that urea might decompose nitrous acid as an NO_x absorption product, if nitrite ion was present at higher concentrations.

In order to understand the mechanism of NO_x absorption by Na_2SO_3 solution, a material balance was made for two reactors operating at the same conditions, one containing pure water and another an 8 gm/liter Na_2SO_3 solution as shown in experiment 9.

EXP. 9

Both reactor were conducted for 20 min under the following conditions:

volume of the reactor: 500 ml

gas mixture: air + 7000 ppm NO_x (3400 ppm NO and 3600 ppm NO_2)

flow rate: 460 ml/min

temperature: 20°C

The outlet concentrations were:

NO_x = 3000 ppm for pure water

NO_x = 1800 ppm for Na_2SO_3 solution

After 20 min the liquid in the reactors was analyzed for concentrations of nitrite and nitrate ions. The following concentrations were obtained in units of ppm by weight:

- Pure water

$$/\text{NO}_3^-/ = 82 \text{ ppm}$$

$$/\text{NO}_2^-/ = 80 \text{ ppm}$$

- Na_2SO_3 solution

$$/\text{NO}_3^-/ = 75 \text{ ppm}$$

$$/\text{NO}_2^-/ = 145 \text{ ppm}$$

A material balance over NO_x was made to prove the relationship:

$$\text{input} - \text{output} = \text{accumulation}$$

- Pure water

$$\begin{aligned} \text{input} - \text{output} &= q \cdot t \cdot (/\text{NO}_x/_\text{in} - /\text{NO}_x/_\text{out}) \cdot M_{\text{NO}_x} \\ &= 460 \frac{\text{ml}}{\text{min}} \cdot 20 \text{ min} \cdot 10^{-6} (7000 - 3000) \frac{1 \text{ atm}}{82.06 \frac{\text{ml} \cdot \text{atm}}{\text{gmol} \cdot ^\circ\text{K}} \cdot 293^\circ\text{K}} \cdot 38 \frac{\text{gm}}{\text{gmol}} \\ &= \underline{0.058 \text{ gm}} \end{aligned}$$

$$\begin{aligned} \text{accumulation} &= /\text{NO}_3^-/ \frac{V M_{\text{NO}_3^-}}{\rho_w M_{\text{NO}_3^-}} + /\text{NO}_2^-/ \frac{V M_{\text{NO}_2^-}}{\rho_w M_{\text{NO}_2^-}} \\ &= 80 \cdot 10^{-6} \cdot 500 \text{ ml} \cdot 1 \frac{\text{gm}}{\text{ml}} \frac{38}{62} + 82 \cdot 10^{-6} \cdot 500 \text{ ml} \cdot 1 \frac{\text{gm}}{\text{ml}} \frac{38}{46} \\ &= \underline{0.058 \text{ gm}} \end{aligned}$$

- Na₂SO₃ solution

$$\text{input} - \text{output} = 460 \cdot 20 \cdot 10^{-6} (7000 - 1800) \frac{1}{82.06 \cdot 293} 38$$

$$= \underline{0.076 \text{ gm}}$$

$$\text{accumulation} = 75 \cdot 10^{-6} \cdot 500 \cdot \frac{38}{62} + 145 \cdot 10^{-6} \cdot 500 \cdot \frac{38}{46}$$

$$= \underline{0.081 \text{ gm}}$$

q - gas flow rate, ml/min

t - time, min

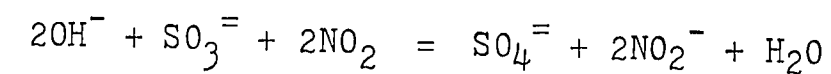
ρ_w - density of water - 1 gm/ml

V - volume of the liquid in the reactor

M_{NO_x} , M_{NO_2} , M_{NO} - molecular weights

The NO_x molecular weight is taken as 38, an average value of M_{NO} and M_{NO_2} since the NO and NO_2 concentrations in the inlet stream were approximately the same. This is not true for the outlet stream but the error is assumed not to be significant.

The material balance showed that all the NO_x that was absorbed was in both cases converted to either nitrate or nitrite. Using pure water the distribution is about 50% nitrite and 50% nitrate and using Na_2SO_3 solution it is about 35% nitrate and 65% nitrite (by weight). Since the nitrate concentration did not change much when sulfite was added, there are good reasons to believe that SO_3^{2-} solution absorbs NO_2 only, according to reaction:



and that the decrease in NO concentration is due to better oxidizing action of oxygen in the presence of sulfite ions.

5. SULFITE TO SULFATE OXIDATION

A simple quantitative model for sulfite to sulfate oxidation is developed based on a fast reaction between SO_3^- and oxygen in which case the concentration of the reaction product (sulfate) will be large in the liquid at the bubble surface (where the reaction occurs) and will attain saturation there with the result that the rate controlling step will become the diffusion of the sulfate product away from the gas bubble into the bulk liquid.

The following notation is used:

- C_b - concentration of SO_4^- in the bulk, moles/liter
- C_{b0} - the initial SO_4^- concentration, moles/liter
- C_o - the initial SO_3^- concentration, moles/liter
- C_s - the saturation concentration of SO_4^- in water, moles/liter
- C - concentration of SO_3^- in the bulk, moles/liter
- V - volume of the reactor, liter
- t - time, min
- A - surface area of all the bubbles in the reactor, cm^2
- k - overall mass transfer coefficient, cm/min

We assume that the rate of disappearance of sulfite is equal to the sulfate diffusion rate:

$$-\frac{dC}{dt} = \frac{A \cdot k}{V} (C_s - C_b) \quad (1)$$

The SO_4^- concentration in the bulk increases during time:

$$C_b = C_{b0} + C_o - C \quad (2)$$

Substituting (2) into (1) :

$$\frac{dC}{dT} = - \frac{A \cdot k}{V} (C_S - C_{b0} - C_O + C) \quad (3)$$

This can be integrated assuming that k is constant, although it does change with concentration but the change is assumed to be negligible.

$$\frac{1}{C_S - C_O - C_{b0}} \int_{C_O}^C \frac{dC}{1 + \frac{C}{C_S - C_O - C_{b0}}} = - \frac{A \cdot k}{V} \int_0^t dT$$

Integrating:

$$\ln \frac{1 + \frac{C}{C_S - C_O - C_{b0}}}{1 + \frac{C_O}{C_S - C_O - C_{b0}}} = - \frac{A \cdot k}{V} t$$

$$t = \frac{V}{A \cdot k} \ln \frac{C_S - C_{b0}}{C_S - C_O - C_{b0} + C}$$

From here the sulfite life time can be calculated by setting $C=0$, provided A and k are known. The model can be tested by measuring the sulfite concentration as the experiment progresses and plotting time against $\ln(C_S - C_{b0} / C_S - C_O - C_{b0} + C)$ which should be a straight line if the model agrees with the experimental data. This was done in the following experiments.

EXP. 1

For sodium sulfate in water, $C_S = 1.37$ moles/liter. In this experiment C_O was taken as 1.37 moles/liter, with $C_{b0} = 0$, so that (4) simplifies to:

$$t = \frac{V}{A \cdot k} \ln \frac{1.37}{C}$$

The air was bubbled through the sulfite solution in a 500 ml bubbler at the rate of 1300 ml/min and a temperature of 20°C. The sulfite concentration was monitored by measuring the pH of the solution. The values of concentrations were obtained from a calibration chart (Figure 6.) of concentration vs. pH.

| | | | | |
|----------------------|------|------|------|-------|
| time, min | 0 | 10 | 20 | 35 |
| pH | 10 | 9.75 | 9.55 | 9.30 |
| C, gm/liter | 172 | 60 | 28 | 11 |
| C, mol/liter | 1.37 | 0.48 | 0.22 | 0.087 |
| $\ln \frac{1.37}{C}$ | 0 | 1.05 | 1.82 | 2.76 |

The results are plotted in Figure 7. where it is evident that experimental data fall almost on a straight line. The slight deviation from linearity can be explained in terms of slower chemical reaction rates at the lower concentrations and correspondingly larger logarithmic terms plotted in Figure 7. The initial assumption was that chemical reaction was fast. At lower concentrations this might not be true and the measured sulfite life times would then be longer than predicted by the model. That might be the reason that the point at the extreme right hand side in Figure 7. is higher than expected.

However, if we fit a straight line between the first two points the slope is 11 minutes:

$$\frac{V}{A \cdot k} = 11 \text{ min}$$

and:

$$A \cdot k = \frac{500 \text{ cm}^3}{11 \text{ min}} = 45.5 \frac{\text{cm}^3}{\text{min}}$$

To calculate the mass transfer coefficient k we need the surface area of all the bubbles. In bubbling systems the volume fraction

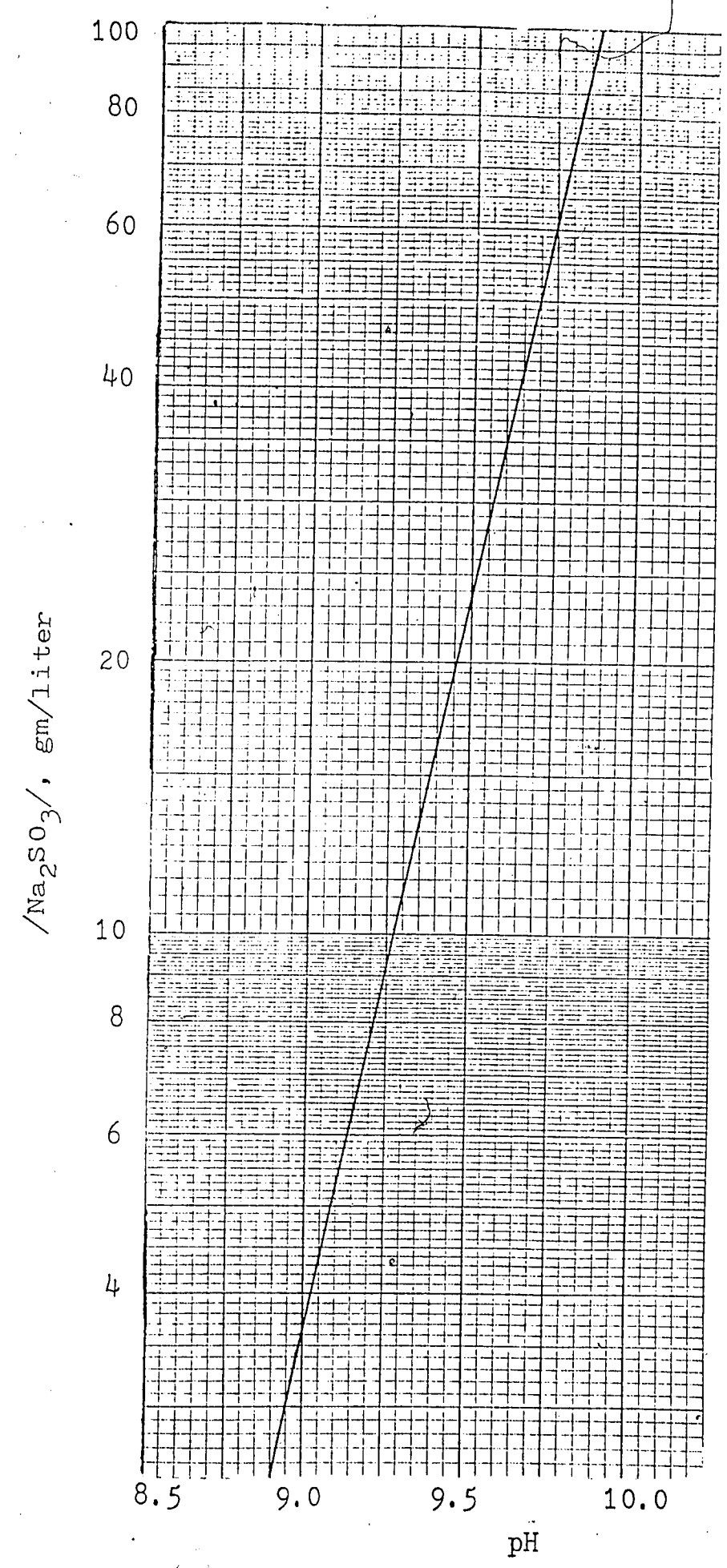


FIGURE 6. Calibration Chart of Na_2SO_3 vs. pH

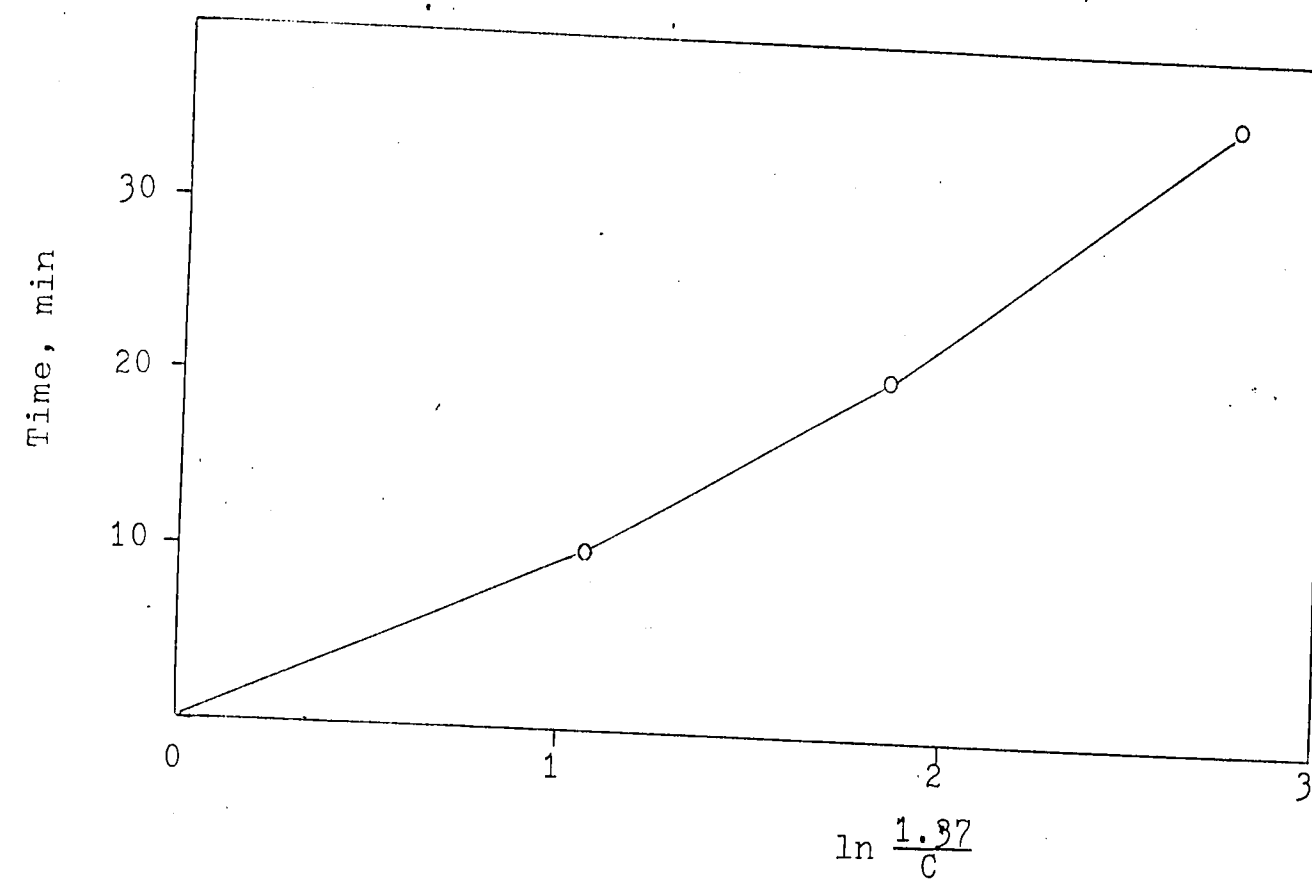


FIGURE 7. Time vs. $\ln (1.37/C)$
Exp. 1

of bubbles is between 5 and 10 percent, so assuming the later value we get the volume of all the bubbles:

$$V = 500 \cdot 0.1 = 50 \text{ cm}^3$$

and surface area:

$$A = \frac{3 \cdot V}{r}$$

where r is an average bubble radius. Assuming r equals 1 mm we get:

$$A = \frac{3 \cdot 50}{0.1} = 1500 \text{ cm}^2$$

Then:

$$k = \frac{A \cdot k}{A} = \frac{45.5}{1500} = 0.03 \text{ cm/min}$$

$$k = 5.0 \cdot 10^{-6} \text{ m/sec}$$

EXP 2.

Another experiment was done with an initial value of $\text{SO}_4^{=}$ concentration in the bulk: $C_{b0} = 0.37$ moles/liter. The value of C_0 is taken as 1 mol/liter so that (4) simplifies to:

$$t = \frac{V}{A \cdot k} \ln \frac{1}{C}$$

With the same conditions as in Exp. 1. the following results are obtained:

| | | | | | | | |
|-------------------|------|------|------|------|------|------|------|
| time, min | 0 | 10 | 20 | 30 | 40 | 50 | 60 |
| pH | 9.95 | 9.75 | 9.60 | 9.45 | 9.40 | 9.15 | 9.05 |
| C, gm/liter | 126 | 60 | 34 | 19 | 16 | 6.3 | 4.4 |
| C, mol/liter | 1 | 0.48 | 0.27 | 0.15 | 0.13 | 0.05 | 0.03 |
| $\ln \frac{1}{C}$ | 0 | 0.72 | 1.31 | 1.90 | 2.06 | 3.0 | 3.3 |

The results are plotted in Figure 8.

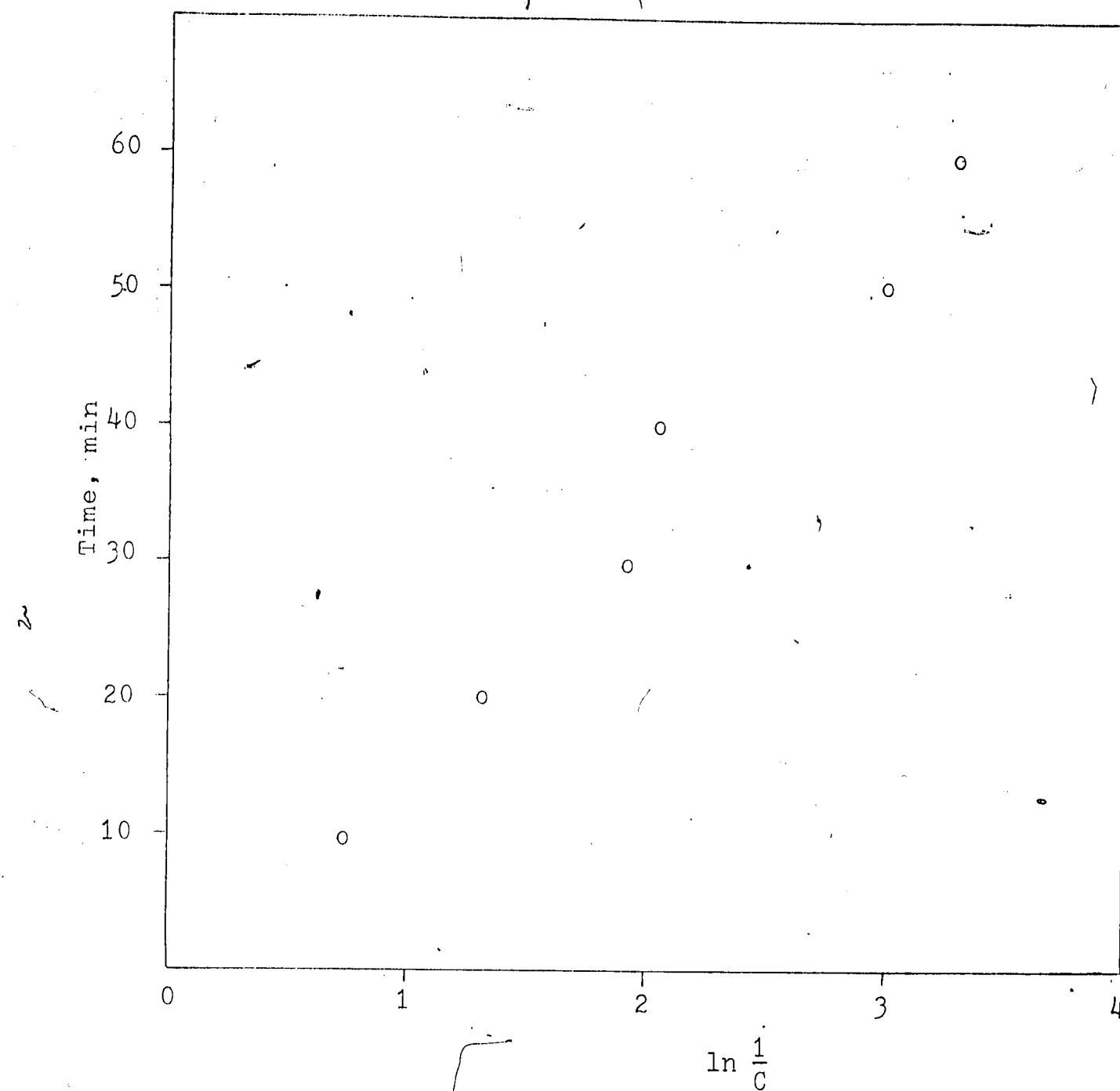


FIGURE 8. Time vs. $\ln \frac{1}{C}$
Exp. 2

The foregoing model and experimental data suggest that the sulfite oxidation rate can be slowed down by reducing the diffusion driving force for transport of $\text{SO}_4^{=}$ product away from the site of reaction at the bubble surface. This is easily done by adding sulfate to the bulk.

In Exp 8. of Chapter 4. the sulfite life time was about 20 min at 70°C . When 100 gm of Na_2SO_4 were added to the sulfite solution at the same temperature and flow rate as in Exp 8., the sulfite life time increased to 130 min showing that the oxidation of sulfite can be retarded by this simple expedient.

6. CONCLUSION AND RECOMMENDATIONS FOR FUTURE RESEARCH

An aqueous wet scrubbing process using SO_3^- ion for removing NO_x from flue gases appears promising, since sulfite ion seems to promote sorption of both NO_2 and NO , provided oxygen is also present. The future work should be aimed at determining the minimal O_2/N_2 ratio in the gas stream which can still give a satisfactory NO_x absorption rate. The amount of NO_x , or better NO , absorbed should be measured for different O_2/N_2 ratios and different SO_3^- concentrations at room temperature showing how these parameters affect the overall process. Later on, different temperatures and pressures might be investigated as well as the urea-nitrous acid reaction in presence of a catalyst.

The SO_2 absorption is enhanced by adding CO to the gas stream. As mentioned before, the future experiments should attempt to explain the mechanism of the CO action. A possibility of forming metal carboniles and their possible role as catalysts should be investigated also.

The overall process might then include SO_2 absorption and catalytic reduction to elemental sulfur with usage of the intermediate product, sulfite, to remove nitrogen oxides in a form of nitrate or nitric acid.

LITERATURE CITED

1. Ludwig, J. H., and P. W. Spaite, Chem. Eng. Prog. 63 (6) 82 (1967).
2. Fritz, J. S., and S. S. Yamamura, Analytical Chemistry, Vol. 27, No. 9, 1955.
3. Lepsoe, R., Ind. Eng. Chem. 30, 1938.
4. Hall, W. T., Analytical Chemistry, Vol. 1.
5. George, D. R., Crocker, L., and Rosenbaum, J. B., Min Engr. 22 (1), 75 (1970).
6. Barthel, Y., " IFP processes for recovering H_2S and SO_2 from Claus unit tail gas, and for cleaning SO_2 from stack gas ", A.P.C.A. annual meeting, Chicago, June 1973.
7. Saleem, A., and Sheehan, J. D., "Application of the phosphate process to a large utility boiler", A. P. C. A. annual meeting, Boston, 1975.